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PARAMAGNETIC RESONANCE OF THE TRIPOSITIVE
CURIUM ION IN ETHYLSULFATE AND TRICHLORIDE
CRYSTALS

Berkeley, California

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Marvin Abraham, B. R. Judd, and H. H. Wickman

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ION IN ETHYLSULFATE AND TRICHLORIDE CRYSTALS*Marvin Abraham,[†] B.R. Judd,[‡] and H.H. WickmanLawrence Radiation Laboratory
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A few years ago, the paramagnetic resonance spectrum of Cm^{3+} substituted for La^{3+} in the crystal LaCl_3 was reported by a group at Berkeley¹ and, with apparently greater precision, by a group at the Argonne National Laboratory.² Seven lines were observed, characteristic of a level with a total angular momentum, J , of $7/2$, and a Landé g value of 1.991. These results received a ready explanation. The ground state of Cm^{3+} was expected to be $5f^7 \ ^8S_{7/2}$, and the spectrum of the rare-earth analog, $\text{Gd}^{3+} 4f^7 \ ^8S_{7/2}$, had already been found to comprise seven lines for which $g = 1.991$.³ From the spread of the seven lines with respect to the external magnetic field, it was concluded that the zero-field splitting of $\ ^8S_{7/2}$ of Cm^{3+} was very similar to that of $\ ^8S_{7/2}$ of Gd^{3+} , though the Argonne group stated that the two spectra were sufficiently dissimilar to be easily distinguished.²

As our knowledge of the actinides has increased, the similarity between the reported spectrum of Cm^{3+} and that of Gd^{3+} has become increasingly embarrassing. The extent of the breakdown of Russell-Saunders coupling should be greater than that for $\text{AmI } 5f^7 \ ^8S_{7/2}$, for which $g = 1.937$.⁴ It should be less than that calculated by Runciman for Cm^{3+} ,⁵ since the recent work of Lämmermann and Conway on PuI indicates that Runciman probably over-estimated the spin-orbit coupling constant.⁶ From Runciman's eigenfunctions, we calculate $g = 1.913$, and hence we would expect the g -value of the ground

level of Cm^{3+} to satisfy the inequality $1.937 > g > 1.913$.

The similarity between the reported zero-field splittings of the ground levels of Gd^{3+} and Cm^{3+} is equally puzzling. Making use of Runciman's eigenfunctions, we find that the ground state of Cm^{3+} comprises only 72% of the pure state $^8\text{S}_{7/2}$, and we should expect it to show the minute zero-field splitting characteristic of the ground level of Gd^{3+} only if a highly fortuitous cancellation of the mechanisms that give rise to the splitting occurs.

With these difficulties in mind, experiments were set up to observe (at 9 kmc.) the paramagnetic resonance spectrum of Cm^{3+} substituted in small amounts for La^{3+} in lanthanum ethylsulfate and in lanthanum trichloride. In all, five ethylsulfate and two trichloride crystals were grown with varying concentrations of Cm^{3+} . After the experiments, the crystals were assayed to determine the Cm^{3+} concentration, which was found to vary between 1 microgram and 20 micrograms. For the ethylsulfate crystals, a single line was observed at helium temperatures, characterized by $g_{\parallel} = 1.925 \pm 0.002$ and $g_{\perp} = 7.73 \pm 0.02$. A similar line was observed in the trichloride crystals, the parameters being $g_{\parallel} = 1.925 \pm 0.002$ and $g_{\perp} = 7.67 \pm 0.02$. No trace was seen of the seven lines previously reported,^{1,2} and it appears quite certain that the spectrum measured earlier was that of Gd^{3+} , not Cm^{3+} .

It is remarkable that two groups, working independently, should have made the same erroneous identification.

The observed spectra receive an immediate explanation if the zero-field splitting of the ground level of Cm^{3+} is supposed to be large compared with the energy of the microwave quantum. The single line observed in all crystals corresponds to transitions between the components of the lowest doublet. If this doublet corresponds to $J_z = \pm \frac{1}{2}$, it is easy to show that $g_{\parallel} = g$ and $g_{\perp} = 4g$. The value of g_{\parallel} is independent of interactions with higher components of the ground level, and we can immediately conclude that $g = 1.925$ for the ground level of Cm^{3+} . This result is consistent with the theory. The values of g_{\perp} are very near the theoretical value of $4g$, the slightly lower value for the trichloride possibly being due to the influence of the doublet for which $J_z = \pm \frac{3}{2}$. Such an effect suggests that the splitting of the ground level of Cm^{3+} is smaller in the trichloride than in the ethylsulfate, a result analogous to that for Gd^{3+} in the two crystals.³ This is also suggested by a number of weak, highly anisotropic, lines in the spectrum of the trichloride, some of which may arise from transitions between higher components of the ground level. These are now being investigated.

The present work, by showing the spurious nature of the earlier observations, eliminates what had become a serious difficulty in the theory; at the same time, it provides an

important datum, namely the Landé g value of the ground level of Cm^{3+} , that should be valuable in fixing the degree of intermediate coupling both for Cm^{3+} and, by extrapolation, for later members of the actinide series.

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